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One Pot Electrooxidative Conversion of Aromatic 1,2-Diketones into Methyl Carboxylates

Mitsuhiro Okimoto,* Yuji Nagata, Satoru Sueda, and Yukio Takahashi

Department of Applied Chemistry and Circumstance
Engineering, Kitami Institute of Technology,
Kitami, Japan

ABSTRACT

One-pot conversion of several aromatic1,2-diketones into the corresponding methyl carboxylates was performed by indirect electrooxidation using iodide ion as an electron carrier in the presence of catalytic amount of sodium cyanide.

Key Words: Electrooxidation; Benzil; Methyl carboxylate; Iodide ion; Cleavage.

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*Correspondence: Mitsuhiro Okimoto, Department of Applied Chemistry and Circumstance Engineering, Kitami Institute of Technology, Koen-cho 165, Kitami 090-8507, Japan; E-mail: oki@chem.kitami-it.ac.jp.

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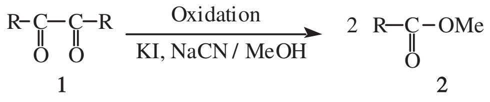
Several studies describing the cleavage of benzil in the presence of cyanide ions have been reported. Trisler and Frey have obtained stilbenediol dibenzoate from benzil by treatment with sodium cyanide in dimethyl sulfoxide.[1] Kwart and Baevsky have treated benzil with cyanide ions in alcoholic solutions to afford cleavage products, benzaldehyde, and the corresponding benzoate.[2] Furthermore, Dakin and Harington have found that benzamide and benzaldehyde are formed as main products by the cleavage of benzil in alcoholic ammonium cyanide solutions.[3] Although cleavage of benzil by cyanide ions has been studied extensively, and is well-known, as mentioned above, complete transformation of 1,2-diketones through electro-oxidation into a single product has yet to be reported, to the best of our knowledge. As a note, we have previously reported on the effective electrooxidative conversion of benzaldehydes into the corresponding methyl carboxylates, in the presence of catalytic amount of sodium cyanide[4] or KI.[5]

As a continuation in our series of studies using electrochemical methods, we have carried out one-pot conversion of 1,2-diketones into two equivalent amounts of methyl carboxylates. During the beginning stages of the experiment, we have confirmed that the utilization of one tenth equivalent of sodium cyanide relative to benzil in MeOH was sufficient to nearly complete the cleavage of benzil into benzaldehyde and methyl benzoate. Moreover, this cleavage reaction occurred within a few minutes at room temperature. In our studies, several 1,2-diketones were cleaved, between the two carbonyl groups, and subsequently electrooxidized to afford the corresponding methyl carboxylates in good to excellent isolated yields (Table 1).

Unexpectedly, the yields of the corresponding methyl carboxylates (**2e**, **2k**) from 2,2′-dimethoxy benzil (**1e**) and 2-pyrizil (**1k**) were only 46 and 43%, respectively. In the former case, cleavage reaction by the cyanide ions was not as efficient, even at elevated temperatures (60°C), and/or with a longer reaction period (6 h). In contrast, in the latter case, although the cleavage reaction proceeded effectively, the subsequent electrooxidation process of the corresponding aldehyde into the methyl carboxylate did not proceed smoothly. Other reaction conditions of the electrooxidation, such as electrode material, halogen ion source, amount of added KI, and reaction temperature were examined using benzil (**1a**) as the standard substrate. To study the electrode material, substituting the platinum net with four pieces of carbon poles (diameter, 5 mm; height, 80 mm) as the anode material resulted in the decrease in the yields of methyl benzoate, from 95 to 82% (yields were determined using GLC analysis), in the case of a lead plate (width, 30 mm; height, 50 mm)

Table 1. One pot conversion of 1,2-diketones into methyl carboxylates.[a]

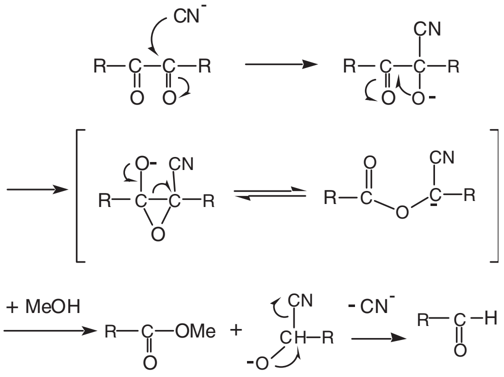


	Substrate *R*	Current passed ($F\,mol^{-1}$)	Yield[b] of **2** (%)
1a	Ph	4.0	80 (95)
1b	4-$CH_3C_6H_4$	4.0	82 (92)
1c	2-$CH_3C_6H_4$	5.7	81 (88)
1d	4-$CH_3OC_6H_4$	6.5	83 (88)
1e	2-$CH_3OC_6H_4$	7.8	46 (53)
1f	4-ClC_6H_4	3.7	93 (98)
1g	2-ClC_6H_4	5.5	85 (94)
1h	4-*tert*-Bu-C_6H_4	5.0	94 (98)
1i	2-Furyl	4.0	86 (93)
1j	2-Thienyl	4.0	83 (93)
1k	2-Pyridil	4.9	43 (55)

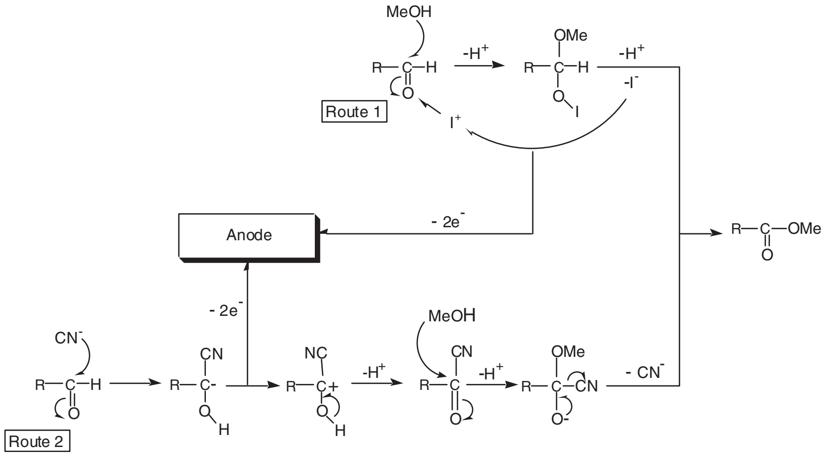
[a] Substrate: 2.5 mmol; KI: 2.0 mmol; NaCN: 0.25 mmol, 0.5 mmol(**1c**), 1.0 mmol(**1d**), 4.0 mmol(**1e**); MeOH: 40 mL; temperature: ca.15°C.
[b] Isolated yield. Values in parentheses are GLC yield.

as the anode, the yield of the methyl benzoate was only 58%, and benzaldehyde remained unreacted (30%). Reactions using alternate halogen sources, such as NaI, I_2, KBr, and KCl, were investigated, resulting in methyl benzoate yields of 90, 88, 47, and 46%, respectively. These results suggested that iodide ions were effective as electron carrier in this oxidation system, relative to the bromide and chloride ions. Investigations have shown that the utilization of 0.8 equiv. of KI for **1a** was sufficient for this indirect electrooxidation. In terms of the reaction temperature, we did not observe significant differences in the yields of methyl benzoate (±4%) between the temperature range of 0–50°C.

Possible reaction pathways of this cleavage reaction and the subsequent oxidation are illustrated in Schs. 1–3. Presumably, the 1,2-diketone molecule was cleaved into the corresponding methyl carboxylate and aldehyde by attack of the cyanide ion at the first step of the reaction, as shown in Sch. 1, theoretically, methyl carboxylate was already formed in 50% yield in this first reaction step. As the second reaction step, the subsequent electrooxidation of the aldehyde proceeded gradually. In

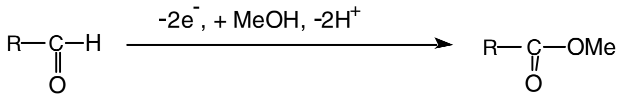


Scheme 1.



Scheme 2.

the presence of either iodide or cyanide ions, we proposed two reaction pathways (Sch. 2, Routes 1 and 2, respectively), as based on our previous studies.[4,5] Route 1 is the indirect electrooxidation of the aldehyde by the action of the iodine cationic species, which were formed through a two-electron transfer of the iodide ion on the anode. Route 2 is the direct oxidation of cyanohydrin derivative, which was formed by the reaction of the aldehyde with cyanide ions to afford benzoyl nitrile through a two-electron transfer on the anode. We had previously conformed that benzoyl nitrile readily reacted with MeOH to give methyl benzoate, even



Scheme 3.

at room temperature.[6] On the other hand, we also observed that some aromatic aldehydes could be converted into the corresponding methyl carboxylates in ca. 85% yield after passing 2.3 F/mol of electricity under the same reaction conditions employed in this study.

In our opinion, Route 1 is strongly preferred over Route 2, since the oxidation potential of iodide ions is much lower than that of cyanohydrin derivative,[7] and in fact, in the absence of KI, methyl carboxylates could not be obtained in such high yields. Shortened versions of both reaction routes presented in Sch. 2 are illustrated in Sch. 3. In conclusion, we have established a one-pot conversion of 1,2-diketones into the corresponding methyl carboxylates under very mild conditions by utilizing the electrochemical technique with catalytic amounts of cyanide and iodide ions.

EXPERIMENTAL

All electrooxidation products (**2a–2k**) were identified by comparison of their physical and spectral data with those of authentic samples. The substrates were prepared by the usual oxidation reactions[8] of the corresponding acyloines, which were provided by the typical benzoin condensations[9] of the corresponding aldehydes. Other reagents were obtained from commercial suppliers and used without further purifications. Preparative-scale electrooxidations were carried out in a tall 50 mL beaker equipped with a fine frit cup as the cathode compartment, a cylindrical platinum net anode (diameter, 33 mm; height, 40 mm), and a nickel coil cathode. 1,2-Diketones **1a–1k** were oxidized under conditions as follow: a solution of substrate **1a–1k** (2.5 mmol), KI (2.0 mmol), and NaCN (0.25 mmol, 0.5 mmol for **1c**, 1.0 mmol for **1d**) in MeOH (40 mL) was electrooxidized under a constant current (0.2 A). During the course of the electrooxidation, the anolyte was magnetically stirred, and the temperature of the cell was maintained at approximately 15°C. After completion of the electrooxidation, the reaction mixture was treated using a three fold amount of the anolyte solution. After concentrating the combined anolyte solution in vacuo at approximately 30°C to roughly one-fifth of its original volume, the resulting residue was treated with water (60 mL), and the oily layer was extracted with ether (3 × 40 mL). The combined ether extracts were washed with aqueous sodium thiosulfate solution (20 wt%, 20 mL), and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by distillation or by column chromatography (diameter, 3.5 cm; height, 25 cm) on silicagel using ether as the eluent.

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